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**Dispersion of  $\chi(3)$  in Polydiacetylene Films from  
Electroabsorption Spectroscopy**

**by**

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Dispersion of  $\chi^{(3)}$  in Polydiacetylene Films from  
Electroabsorption Spectroscopy

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**Abstract**

Electroabsorption spectroscopy was carried out on a polydiacetylene, poly{[[8-butoxy carbonyl] methyl urethanyl] 1-(5-pyrimidyl) -octa-1, 3-diyne} (poly(BPOD)) film from 470nm to 730nm, and on a polydiacetylene poly-(butoxycarbonylmethyleneurethane) (poly(4-BCMU)) film from 400nm to 700nm. The dispersion of the imaginary part of the complex  $\chi_{\text{eff}}^{(3)}$ , which is a combination of  $\chi_{1133}^{(3)}(\omega; \omega, 0, 0)$  and  $\chi_{3333}^{(3)}(\omega; \omega, 0, 0)$ , was directly determined from experiment. The real part of  $\chi_{\text{eff}}^{(3)}$  was calculated from its imaginary part by Kramers-Kronig relation. The complex susceptibilities  $\chi_{1133}^{(3)}(\omega; \omega, 0, 0)$  and  $\chi_{3333}^{(3)}(\omega; \omega, 0, 0)$  were thus obtained from  $\chi_{\text{eff}}^{(3)}$  determined at normal and tilted incidence. The results for both polydiacetylene spin coated films satisfy  $\chi_{3333}^{(3)} \approx 1.5 \chi_{1133}^{(3)}$ , and are significantly different from the relation  $\chi_{3333}^{(3)} = 3\chi_{1133}^{(3)}$ , expected for an isotropic film. It indicates that the polymer chain segments in both polydiacetylene films lie mainly on the film

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plane instead of an isotropic distribution. The  $\chi^{(3)}$  values for both materials are of the order of  $10^{-11}$  esu. Some enhancement of nonlinearity of poly(BPOD) over poly(4-BCMU) is observed.

## I. Introduction

Polydiacetylenes(PDAs) are known to possess large 3rd order nonlinear susceptibilities due to their delocalized  $\pi$  electrons along the backbone[1]. Their electronic and optical properties, and processability can be further modified by altering the side groups attached to the main backbone[2]. Therefore, they have attracted great attention as potential electronic and optical material. A number of experiments have been performed to investigate the behavior of  $\chi^{(3)}$  of poly(4-BCMU)[3,4,5,6,7], which is a solution processable polydiacetylene( see Figure 1(a) for its structure ). However, complete  $\chi^{(3)}$  spectra of this material from electroabsorption measurements have not been reported yet. Other electroabsorption experiments on polydiacetylenes have been carried out to infer their electronic energy levels[8].

It has been reported that PDAs with aromatic side groups conjugated to the back-bone will possess enhanced nonlinear optical property due to the increase of the number of  $\pi$  electrons per repeat unit[2,9,10]. Recently, Kim et al.[11] have synthesized a new aromatic substituted polydiacetylene, poly{[[8-butoxy carbonyl] methyl urethanyl] 1-(5-pyrimidyl)-octa-1, 3-diyne}, namely poly(BPOD), in which an aromatic side group is used to substitute a side group of poly(4-BCMU) (see Figure 1(b) ). This new class of polydiacetylene is soluble in common organic solvents, and good optical quality films of poly(BPOD) can be cast or spin coated from polymer solutions. The absorption spectrum of poly(BPOD) is red shifted in solution, showing increased  $\pi$  electron delocalization compared to poly(4-BCMU). In addition, appreciable second order nonlinearity has been observed in spin coated films without poling[12]. Acentric organization was achieved due to self assembly of the molecules in the bulk. Therefore, it is very interesting to compare the third order nonlinearity of poly(BPOD)

with that of poly(4-BCMU), and enhancement of the third order nonlinearity of poly(BPOD) is expected due to the aromatic side group.

Electroabsorption spectroscopy can determine the dispersion of each  $\chi^{(3)}$  component and can provide information about chromophore orientation in the material. The normal incidence of electroabsorption can determine the imaginary part of the change of refractive index  $\delta\kappa$  which is due to the applied electric field and is associated with the component  $\chi_{1133}^{(3)}$ . By using Kramers-Kronig relation[13], the real part of the change of the refractive index  $\delta n$  can be determined. The complex value of  $\chi_{1133}^{(3)}$  is subsequently determined. Similarly, electroabsorption at tilted incidence can determine the complex value  $\chi_{\text{eff}}^{(3)}$ , which is composed of  $\chi_{1133}^{(3)}$  and  $\chi_{3333}^{(3)}$ . Thus  $\chi_{3333}^{(3)}$  can be uniquely determined from these measurements. The obtained ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  can be utilized to offer information about the arrangement of the chromophores in the polymer film. If the chromophore can be treated as a microscopic one dimensional rod like unit, then,  $\frac{\chi_{3333}^{(3)}}{\chi_{1133}^{(3)}} < 3$  indicates that the chromophores are inclined to lie along the film plane, and  $\frac{\chi_{3333}^{(3)}}{\chi_{1133}^{(3)}} = 3$  indicates that the chromophores are isotropically oriented in three dimensional space, and  $\frac{\chi_{3333}^{(3)}}{\chi_{1133}^{(3)}} > 3$  indicates that the chromophores are inclined to maintain perpendicular to the film plane.

## II. Theoretical Background of the Experiment

Let us consider the case of tilted incidence of electroabsorption spectroscopy(see Figure 2. for the experimental setup). Suppose the optical field inside the sample is  $\vec{E} = \vec{E}(\vec{r})e^{-i\omega t}$ , where  $\vec{E}(\vec{r}) = E_0 \hat{e} e^{i\vec{k} \cdot \vec{r}}$ ,  $E_0$  is the intensity at  $r=0$ ,  $\hat{e}$  is the polarization. The attenuation of the amplitude is given by the imaginary part of wave vector  $\vec{k}$ . We have the nonlinear equation:

$$\nabla^2 \bar{E}(\vec{r}) + \frac{\omega^2}{c^2} \tilde{n}^2 \bar{E}(\vec{r}) = -\frac{4\pi\omega^2}{c^2} \bar{P} \quad (1)$$

where  $\tilde{n}$  is the complex refractive index of the absorptive sample (neglect the birefringence) .

$$\bar{P} = \bar{P}^{(2)} + \bar{P}^{(3)} \quad (2)$$

where  $\bar{P}^{(2)}$  and  $\bar{P}^{(3)}$  are the polarization generated from 2nd and 3rd order of nonlinearities.

$$P_i^{(2)} = 2 \sum_{jk} \chi_{ijk}^{(2)}(-\omega; \omega, 0, 0) e_j \delta_{zk} E_0 E_{ac} e^{ik \cdot \vec{r}} \quad (3)$$

$$P_i^{(3)} = 3 \sum_{jk\ell} \chi_{ijk\ell}^{(3)}(-\omega; \omega, 0, 0) e_j \delta_{zk} \delta_{z\ell} E_0 E_{ac}^2 e^{ik \cdot \vec{r}} \quad (4)$$

where 2 and 3 denote the permutation of the fields[13,14]. The signal at modulation frequency is generated by  $\bar{P}^{(2)}$ , and the signal at twice of the modulation frequency is generated by  $\bar{P}^{(3)}$ .

$\vec{E}_{ac} = E_{ac} \hat{z} = \hat{z} E_{aco} \cos \Omega t$  stands for the applied electric field, where  $\Omega$  is the angular frequency of the applied electric field( $\Omega \ll \omega$ ), and  $\hat{z}$  is defined as the direction of the film normal(see Figure 2). The electric field is treated as a static field. The equation could be written as :

$$\nabla^2 \hat{e} \cdot \bar{E}(\vec{r}) + \frac{\omega^2}{c^2} \tilde{n}^2 \hat{e} \cdot \bar{E}(\vec{r}) = -\frac{4\pi\omega^2}{c^2} \hat{e} \cdot \bar{P} \quad (5)$$

$$\text{where } \hat{e} \cdot \bar{P} = 3\chi_{eff}^{(3)} E_{ac}^2 \hat{e} \cdot \bar{E}(\vec{r}) + 2\chi_{eff}^{(2)} E_{ac} \hat{e} \cdot \bar{E}(\vec{r}) \quad (6)$$

$$\text{with } \chi_{eff}^{(3)} = \sum_{ij} \chi_{ijzz}^{(3)}(-\omega; \omega, 0, 0) e_i e_j, \text{ and } \chi_{eff}^{(2)} = \sum_{ij} \chi_{ijz}^{(2)}(-\omega; \omega, 0) e_i e_j .$$

$$\text{Finally, we have : } \nabla^2 \hat{e} \cdot \bar{E}(\vec{r}) + \frac{\omega^2}{c^2} \tilde{n}_{eff}^2 \hat{e} \cdot \bar{E}(\vec{r}) = 0 \quad (7)$$

$$\text{where } \tilde{n}_{eff}^2 = \tilde{n}^2 + \delta \tilde{n}^2 . \quad (8)$$

$$\text{with } \delta \tilde{n}^2 = 4\pi(2\chi_{eff}^{(2)} E_{ac} + 3\chi_{eff}^{(3)} E_{ac}^2) \quad (9)$$

The optical field sees an effective refractive index  $\tilde{n}_{\text{eff}}$ . Then  $\vec{k} \cdot \vec{k} = \frac{\omega^2}{c^2} \tilde{n}_{\text{eff}}^2$ . The problem is thus reduced to the form given in linear optics. Snell's law gives:  $n_0 \sin \theta_0 = \tilde{n}_{\text{eff}} \sin \theta_{\text{eff}}$ , where  $\theta_{\text{eff}}$  is the complex angle of propagation inside the sample with the applied electric field,  $n_0 = 1$ ,  $\theta_0$  is the angle of incidence in the air. It also gives  $k_y = k_{y0} = 0$  and  $k_x = k_{x0} = \frac{\omega}{c} \sin \theta_0$ . We have:

$$k_z^2 = \vec{k} \cdot \vec{k} - k_x^2 - k_y^2 = \left( \frac{\omega}{c} \right)^2 \left( \tilde{n}_{\text{eff}}^2 - n_0^2 \sin^2 \theta_0 \right)$$

$$\text{i.e. } k_z = \frac{\omega}{c} \left( \tilde{n}^2 - n_0^2 \sin^2 \theta_0 + \delta \tilde{n}^2 \right)^{\frac{1}{2}} \quad (10)$$

where we choose  $\text{Im } k_z > 0$  to give the correct attenuation.

Strictly speaking,  $\theta_{\text{eff}}$  should be determined by Snell's law, which gives:  $n_0^2 \sin^2 \theta_0 = \tilde{n}_{\text{eff}}^2 \sin^2 \theta_{\text{eff}} = (\tilde{n}^2 + \delta \tilde{n}^2) \sin^2 \theta_{\text{eff}}$ . Since  $\delta \tilde{n}^2 \ll 1$  for most cases, we therefore neglect the term  $\delta \tilde{n}^2$  in the determination of  $\theta_{\text{eff}}$ , i.e. we use the complex angle  $\theta$  without the applied electric field, which is determined by  $n_0 \sin \theta_0 = \tilde{n} \sin \theta$ , as the first order approximation for  $\theta_{\text{eff}}$ . Thus  $\hat{e}$  can be obtained from  $\hat{e} \cdot \vec{k} = 0$ , which gives  $\hat{e} = (\cos \theta, 0, -\sin \theta)$  for p polarization.

Both films show  $c_{\infty 0}$  symmetry, and we have confirmed that  $\chi_{xzzz}^{(3)} = \chi_{yzzz}^{(3)} = \chi_{yxzz}^{(3)} = \chi_{xyzz}^{(3)} = 0$  in experiment. Therefore, the nonvanishing  $\chi^{(3)}$  terms for sandwich geometry are  $\chi_{1133}^{(3)}$  and  $\chi_{3333}^{(3)}$ , and  $\chi_{\text{eff}}^{(3)} = \chi_{1133}^{(3)} \cos^2 \theta + \chi_{3333}^{(3)} \sin^2 \theta$ . Similarly, we can prove that  $\chi_{\text{eff}}^{(2)} = \chi_{113}^{(3)} \cos^2 \theta + \chi_{333}^{(3)} \sin^2 \theta$ .

Because the output intensity  $I$  is proportional to  $|e^{ik_z t_k}|^2$  ( $k_y = 0$  and  $k_x$  is real), the change of output intensity  $\Delta I$  due to the applied electric field is given by:

$$\frac{\Delta I}{I} = \frac{\left| e^{ik_z t_k} \right|^2_{E_{\text{ac}} \neq 0}}{\left| e^{ik_z t_k} \right|^2_{E_{\text{ac}} = 0}} - 1 \quad (11)$$

where  $t_k$  is the thickness of the film.

It can be proved by applying (9) and (10) to (11) that

$$\frac{\Delta I}{I} = -4\pi \cdot \frac{\omega}{c} t_k E_{ac}^2 \cdot 3 \operatorname{Im}\left(\frac{\chi_{\text{eff}}^{(3)}}{\tilde{n} \cos \theta}\right) - 4\pi \cdot \frac{\omega}{c} t_k E_{ac} \cdot 2 \operatorname{Im}\left(\frac{\chi_{\text{eff}}^{(2)}}{\tilde{n} \cos \theta}\right) \quad (12)$$

When the lock-in amplifier is set at  $f$  mode ( $\Omega = 2\pi f$ ), it only detects the signal varying as  $\cos \Omega t$ , the relative change of the detected intensity at the modulation frequency  $\Delta I_\Omega$  is given by

$$\frac{\Delta I_\Omega}{I} = -4\pi \cdot \frac{\omega}{c} t_k E_{aco} \cdot 2 \operatorname{Im}\left(\frac{\chi_{\text{eff}}^{(2)}}{\tilde{n} \cos \theta}\right) \quad (13)$$

Equation (13) is used to estimate the order of magnitude of  $\chi^{(2)}$  at normal incidence ( $\theta = 0$ ).  $\frac{\Delta I_\Omega}{I} = -4\pi \cdot \frac{\omega}{c} t_k E_{aco} \cdot 2 \operatorname{Im}\left(\frac{\chi_{113}^{(2)}}{\tilde{n}}\right)$  for normal incidence.

When the lock-in amplifier is set at  $2f$  mode, it only detects the signal varying as  $\cos(2\Omega t)$ . Since  $E_{ac}^2 = \frac{1}{2} E_{aco}^2 \cos(2\Omega t) + \frac{1}{2} E_{aco}^2$ , we therefore replace  $E_{ac}^2$  in (12) with  $\frac{1}{2} E_{aco}^2$  to give the relative change of  $I$  at twice of the modulation frequency  $\Delta I_{2\Omega}$ . That is:

$$\frac{\Delta I_{2\Omega}}{I} = -2\pi \cdot \frac{\omega}{c} t_k E_{aco}^2 \cdot 3 \operatorname{Im}\left(\frac{\chi_{\text{eff}}^{(3)}}{\tilde{n} \cos \theta}\right) \quad (14)$$

The dispersion of  $\operatorname{Im}\left(\frac{\chi_{\text{eff}}^{(3)}}{\tilde{n} \cos \theta}\right)$  is obtained through the measurement of  $\frac{\Delta I_{2\Omega}}{I}$ , and the real part is determined by Kramers-Kronig relation[13], which gives:  $\operatorname{Re}[\chi_{\text{eff}}^{(3)}(\omega)] = \frac{2}{\pi} \int_{\omega_i}^{\omega_f} \frac{\omega' d\omega'}{\omega'^2 - \omega^2} \operatorname{Im}[\chi_{\text{eff}}^{(3)}(\omega')]$ , where  $\chi_{\text{eff}}^{(3)}(\omega) = \frac{\chi_{\text{eff}}^{(3)}}{\tilde{n} \cos \theta}$ ,  $\omega_i$  and  $\omega_f$  are initial and final optical frequencies respectively. Thus the complex dispersion of  $\chi_{\text{eff}}^{(3)}$  can be determined for arbitrary angle of incidence. We can determine  $\chi_{1133}^{(3)}$  and  $\chi_{3333}^{(3)}$  through two different angles of incidence. For p polarization, we have:

$$\chi_{\text{eff}}^{(3)} = \frac{\cos \theta}{\tilde{n}} (\chi_{1133}^{(3)} + \chi_{3333}^{(3)} \tan^2 \theta) \quad (15)$$

At normal incidence,  $\theta = \theta_0 = 0$ , then  $\chi_{\text{eff}}^{(3)}(\theta = 0) = \frac{1}{\tilde{n}} \chi_{1133}^{(3)}$ , and  $\chi_{1133}^{(3)}$  is determined.

At  $\theta_0 = 53^\circ$  for poly(BPOD) (or  $\theta_0 = 52^\circ$  for poly(4-BCMU)),  $\chi_{3333}^{(3)}$  is determined from the expression of  $\chi_{\text{eff}}^{(3)}$ , which gives:

$$\chi_{3333}^{(3)} = \left( \frac{\tilde{n}}{\cos \theta} \chi_{\text{eff}}^{(3)} \right) \Big|_{\theta_0=53^\circ \text{ or } 52^\circ} - \chi_{1133}^{(3)} \left( \frac{\tilde{n}^2}{\sin^2 \theta_0} \right) \Big|_{\theta_0=53^\circ \text{ or } 52^\circ} - 1 \quad (16)$$

By measuring  $\tilde{n} = n + i\kappa$  and determining  $\chi_{\text{eff}}^{(3)}$  through electroabsorption spectroscopy and Kramers Kronig relation,  $\chi_{1133}^{(3)}$  and  $\chi_{3333}^{(3)}$  could be determined without assuming the relation  $\chi_{3333}^{(3)} = 3\chi_{1133}^{(3)}$  appropriate only for isotropic distribution of chromophores.

### III. Experimental

A layer of  $2330^\circ\text{A}$  poly(BPOD) was spin coated on an indium tin oxide(ITO)-glass substrate. A layer of aluminum film ( $\sim 220^\circ\text{A}$ ) was deposited as the top electrode on the poly(BPOD) film after thorough drying. A sinusoidal electric field ( $E_{\text{ac}} = E_{\text{aco}} \cos \Omega t$ ,  $\Omega = 2\pi f$ ,  $f = 1\text{KHz}$ ,  $V_{\text{p-p}} = 25.5\text{V}$ ) was applied to the sample. A beam of p polarized light coming from a tungsten lamp through a monochromator was incident on the sample with the angles of incidence  $53^\circ$  and  $0^\circ$  ( $\theta_0 = 0^\circ$  for normal incidence). The electroabsorption signal  $\Delta I_{2\Omega}$ , which is defined as the change in the output intensity I at twice of the modulation frequency, was detected by the lock-in amplifier in 2f mode. The sign of  $\Delta I_{2\Omega}$  was determined by comparing the amplified signal from lock-in amplifier in 2f mode and the reference signal from the function generator on an oscilloscope. A micro computer was used to control the monochromator and record data from the lock-in amplifier. The experimental setup is shown in Figure 2. For poly(4-BCMU), the experimental conditions were the following: poly(4-BCMU) thickness is  $3506^\circ\text{A}$ ; aluminum electrode thickness  $\sim 300^\circ\text{A}$ ; angles of incidence are  $52^\circ$  and  $0^\circ$ ; Other experimental conditions were same as for poly(BPOD). The

measurement of poly(BPOD) was performed in the wavelength range of 470nm to 730nm with the angle of incidence  $0^\circ$  and  $53^\circ$  respectively. The results of  $\frac{\Delta I_{2\Omega}}{I}$  are shown in Figure 3(a). The peak electroabsorption is at 609nm for both  $0^\circ$  and  $53^\circ$  incidence. The measurement of poly(4-BCMU) was performed from wavelength of 400nm to 700nm with the angle of incidence  $0^\circ$  and  $52^\circ$  respectively. The results of  $\frac{\Delta I_{2\Omega}}{I}$  are shown in Figure 3(b). The peaks of electroabsorption are near 533nm and 560nm for both  $0^\circ$  and  $52^\circ$  incidence.

The dispersions of the real and imaginary part of the complex refractive index  $\tilde{n} = n + ik$  of poly(BPOD) and poly(4-BCMU) were measured by an ellipsometer (Rudolph Research, Type 43603-200E) and a spectrometer (Perkin-Elmer Lambda 9), and are shown in Figure 4.

The electroabsorption signal  $\Delta I_\Omega$  which is defined as the change of the detected intensity at the modulation frequency (f mode), was checked for both materials at normal incidence. For poly(BPOD),  $\frac{\Delta I_\Omega}{I}$  is in the order of magnitude of  $1.3 \times 10^{-4}$ , which gives the order of magnitude of its  $\chi_{113}^{(2)}$  component to be 0.8pm/v. For poly(4-BCMU),  $\Delta I_\Omega$  can not be detected within the range from 400nm to 700nm. We can use the sensitivity of the instrument to give an upper bound of  $\Delta I_\Omega$ , that is  $\frac{\Delta I_\Omega}{I} < 7.3 \times 10^{-6}$ , thus gives the magnitude of  $\chi_{113}^{(2)}$  of poly(4-BCMU) is less than 0.014pm/v.

#### IV. Results and Discussion

The spectra  $\text{Im}(\chi_{1133}^{(3)})$  and  $\text{Im}(\chi_{3333}^{(3)})$  for both films could be explained as coming from red shift of the linear absorption spectrum due to the applied electric field, which makes a single linear absorption peak generate a positive peak at longer wavelength and a negative peak at shorter wavelength in the electroabsorption spectrum. The dispersions of  $\chi_{1133}^{(3)}$  and  $\chi_{3333}^{(3)}$  for both film are shown in Figure 5 and Figure 6. Let us consider the case of poly(BPOD) first. There are two closely situated peaks in the linear absorption spectrum near 530nm and 580nm.

The positive peak generated from the linear absorption peak near 580nm appears near 609nm in  $\text{Im}(\chi_{1133}^{(3)})$  and  $\text{Im}(\chi_{3333}^{(3)})$ . The negative peak generated from the linear absorption peak near 580nm is reduced by superposition with the positive peak generated from the linear absorption peak near 530nm, resulting a negative peak near 575nm in  $\text{Im}(\chi_{1133}^{(3)})$  and  $\text{Im}(\chi_{3333}^{(3)})$ . The negative peak generated from the linear absorption peak near 530nm appears near 525nm in  $\text{Im}(\chi_{1133}^{(3)})$  and  $\text{Im}(\chi_{3333}^{(3)})$ . The same effect is more obvious in poly(4-BCMU). The positive and negative peaks in  $\text{Im}(\chi_{1133}^{(3)})$  and  $\text{Im}(\chi_{3333}^{(3)})$  generated from linear absorption peaks near 485nm and 545nm are separated from each other.

The 3rd order nonlinearity of poly(BPOD) is enhanced compared with poly(4-BCMU) in the sense that the maximum values of  $\chi_{1133}^{(3)}$  and  $\chi_{3333}^{(3)}$  for poly(BPOD) are larger than those of poly(4-BCMU). For poly(BPOD), the maximum value of  $\text{Im}[\chi_{1133}^{(3)}]$  and  $\text{Im}[\chi_{3333}^{(3)}]$  were determined to be  $4.18 \times 10^{-11}$  esu and  $6.25 \times 10^{-11}$  esu at 609nm, the maximum value of  $\text{Re}[\chi_{1133}^{(3)}]$  and  $\text{Re}[\chi_{3333}^{(3)}]$  were determined to be  $-4.15 \times 10^{-11}$  esu and  $-6.40 \times 10^{-11}$  esu at 595nm. For poly(4-BCMU), the maximum value of  $\text{Im}[\chi_{1133}^{(3)}]$  and  $\text{Im}[\chi_{3333}^{(3)}]$  were determined to be  $-3.19 \times 10^{-11}$  esu at 535nm and  $-4.30 \times 10^{-11}$  esu at 533nm respectively, the maximum value of  $\text{Re}[\chi_{1133}^{(3)}]$  and  $\text{Re}[\chi_{3333}^{(3)}]$  were determined to be  $-3.81 \times 10^{-11}$  esu at 547nm and  $-5.82 \times 10^{-11}$  esu at 542nm respectively. The peak positions of poly(BPOD) are shifted from poly(4-BCMU) due to the substituted aromatic side group. The spectra of  $\text{Re}(\chi_{1133}^{(3)})$  and  $\text{Re}(\chi_{3333}^{(3)})$  for both films provide interesting information for possible nonlinear optical applications.

The spectra of  $\chi_{1133}^{(3)}$  and  $\chi_{3333}^{(3)}$  are similar for both films. However, the relation  $\chi_{3333}^{(3)} = 3\chi_{1133}^{(3)}$  is not satisfied for either film. We observe that  $\chi_{3333}^{(3)} \approx 1.5\chi_{1133}^{(3)}$  is instead satisfied for both films for most part of the spectra. We build a model to explain this discrepancy from earlier assumed behavior[15]. The third order nonlinearity is contributed mainly by the  $\pi$  electrons in the backbone of the two polydiacetylenes. Each straight segment of polymer backbone(of the persistence length) could be treated as identical independent one dimensional rodlike chromophore with microscopic third order nonlinearity  $\gamma$  ( $\gamma_{zzzz}$  actually,

where  $z$  means the direction of the rodlike chromophore). The relation  $\chi_{3333}^{(3)} = 3\chi_{1133}^{(3)}$  is based on the 3 dimensional isotropic distribution of these rod like chromophores. However, for spin coated thin films, the distribution of the directions of the polymer chain segments(rodlike chromophores) are not necessarily isotropic in 3 dimensional space. We therefore propose a model that the potential energy of a tilted segment of polymer chain making an angle  $\alpha$  to the film normal is  $U_{\text{chain}}(\alpha) = -U_0 \sin \alpha$ . If we assume the distribution of the angle  $\alpha$  is given by the Boltzmann distribution function, the probability of a segment of polymer chain lying with angle  $\alpha$  to the film normal is proportional to  $\exp[-U_{\text{chain}}(\alpha) / kT] = \exp(p \sin \alpha)$ , where  $p = U_0 / kT$ . For one dimensional chromophore, it can be shown that  $\chi_{1133}^{(3)} \propto \frac{\gamma}{2} \langle \cos^2 \alpha \sin^2 \alpha \rangle$ , and  $\chi_{3333}^{(3)} \propto \gamma \langle \cos^4 \alpha \rangle$  [15,16]. Then we have :

$$\frac{\chi_{3333}^{(3)}}{\chi_{1133}^{(3)}} = \frac{2 \langle \cos^4 \alpha \rangle}{\langle \cos^2 \alpha \sin^2 \alpha \rangle} = \frac{2 \int_0^\pi \exp(p \sin \alpha) \cos^4 \alpha \sin \alpha d\alpha}{\int_0^\pi \exp(p \sin \alpha) \cos^2 \alpha \sin^3 \alpha d\alpha} \quad (17)$$

Computer calculations have shown that when  $p < 0$ , the ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  is larger than 3; when  $p=0$ , the ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  equals to 3; when  $p>0$ , the ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  is less than 3.  $p=3.2$  gives the ratio of 1.5.

We therefore can use the ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  to directly infer information about the chromophore orientation. If the ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  is larger than 3, the chromophores are preferentially inclined perpendicular to the film plane ( $p<0$ ). If the ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  equals to 3, the chromophores are isotropically distributed in the 3 dimensional space ( $p=0$ ). If the ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  is less than 3, the chromophores are preferentially inclined to lie along the film plane ( $p>0$ ).

The ratio of  $\frac{\chi_{3333}^{(3)}}{\chi_{1133}^{(3)}} \approx 1.5$  ( $p=3.2>0$ ) indicates that the polymer chains in both

poly(BPOD) and poly(4-BCMU) films prefer to lie on the film plane instead of adopting 3 dimensional isotropic distribution. This is reasonable since the polymer chains may tend to lie

on the film plane to lower their potential energy when the spin coated film is drying. It would be worth while to determine the ratio of  $\chi_{3333}^{(3)}$  to  $\chi_{1133}^{(3)}$  for other polydiacetylenes.

## V Conclusion

The method of tilted and normal incidence of electroabsorption spectroscopy and Kramers-Kronig relation was used to determine  $\chi_{1133}^{(3)}$  and  $\chi_{3333}^{(3)}$  without using the relation  $\chi_{3333}^{(3)} = 3\chi_{1133}^{(3)}$ . In the cases of poly(BPOD) and poly(4-BCMU), the results do not satisfy the relation  $\chi_{3333}^{(3)} = 3\chi_{1133}^{(3)}$ , which is expected for an isotropic film, instead  $\chi_{3333}^{(3)} \approx 1.5\chi_{1133}^{(3)}$  is established. It indicates that the polymer chain segments(chromophores) in both films preferentially lie on the film plane. The 3rd order nonlinearity of poly(BPOD) is enhanced compared with poly(4-BCMU).

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## Figure Captions

Figure 1. (a) Structure of poly(4-BCMU); (b) Structure of poly(BPOD).

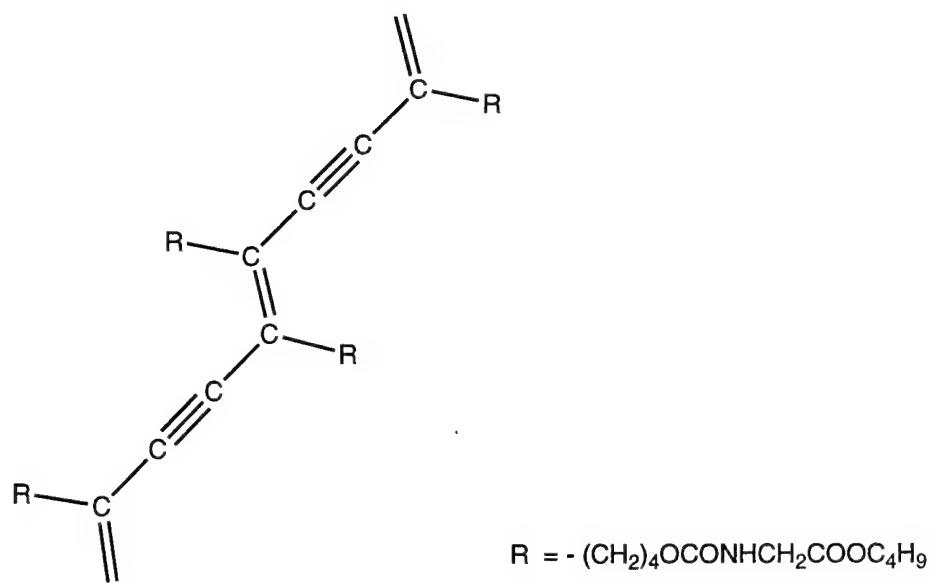
Figure 2. Experimental setup of electroabsorption.

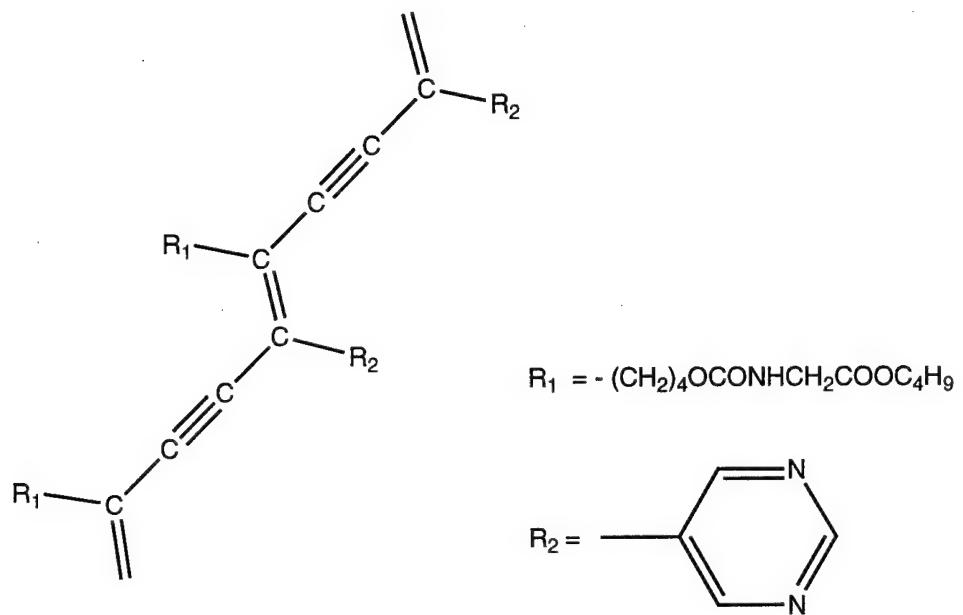
Figure 3. (a)  $\Delta I_{2\Omega}/I$  of normal and tilted incidence for poly(BPOD); (b)  $\Delta I_{2\Omega}/I$  of normal and tilted incidence for poly(4-BCMU).

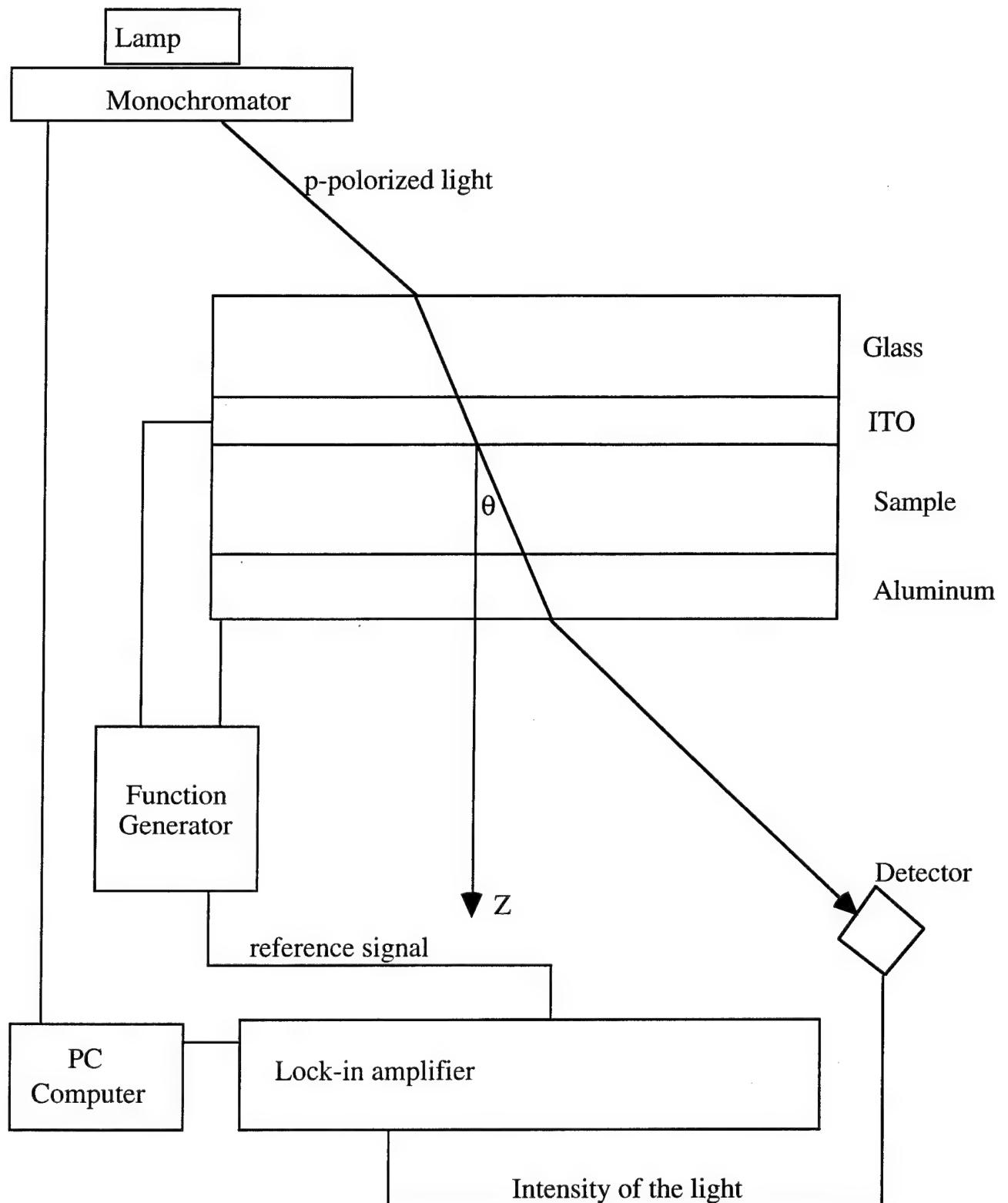
Figure 4. (a) Dispersion of complex refractive index of poly(BPOD); (b) Dispersion of complex refractive index of poly(4-BCMU).

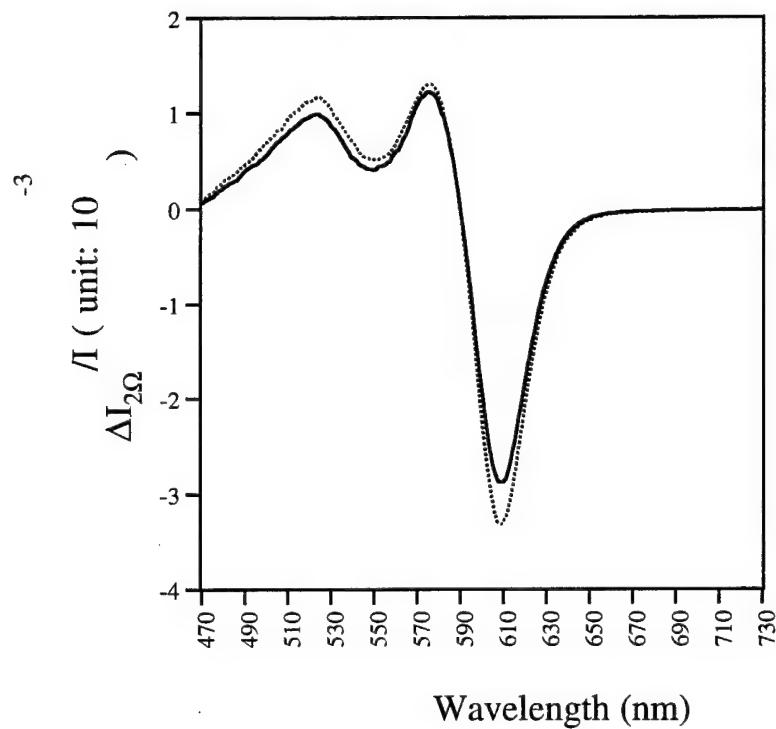
Figure 5. (a) Dispersion of  $\chi_{1133}^{(3)}$  of poly(BPOD). Uncertainty:  $\pm 5.2 \times 10^{-12}$  esu for the real part,  $\pm 2.5 \times 10^{-12}$  esu for the imaginary part. (b) Dispersion of  $\chi_{1133}^{(3)}$  of poly(4-BCMU). Uncertainty:  $\pm 5.3 \times 10^{-12}$  esu for the real part,  $\pm 1.9 \times 10^{-12}$  esu for the imaginary part.

Figure 6. (a) Dispersion of  $\chi_{3333}^{(3)}$  of poly(BPOD). Uncertainty:  $\pm 9.0 \times 10^{-12}$  esu for the real part,  $\pm 3.8 \times 10^{-12}$  esu for the imaginary part. (b) Dispersion of  $\chi_{3333}^{(3)}$  of poly(4-BCMU). Uncertainty:  $\pm 8.1 \times 10^{-12}$  esu for the real part,  $\pm 2.6 \times 10^{-12}$  esu for the imaginary part.

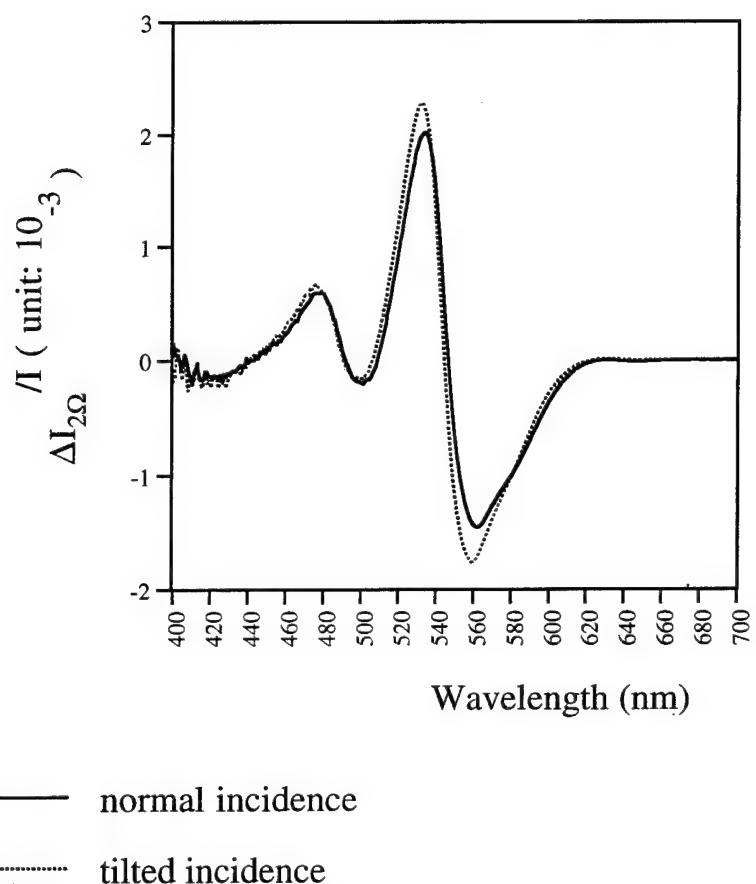


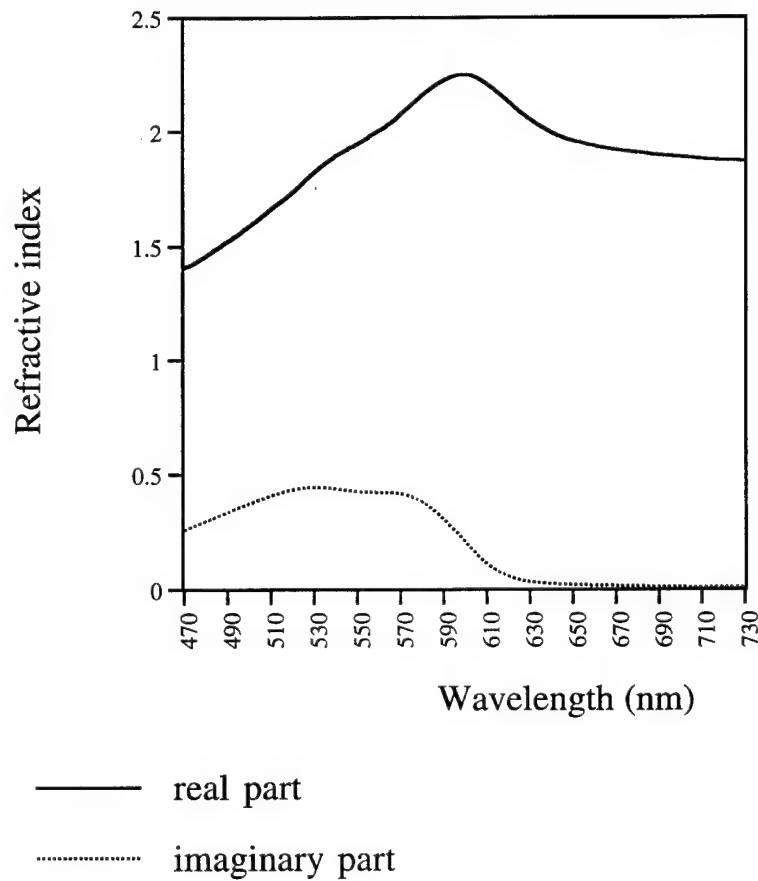


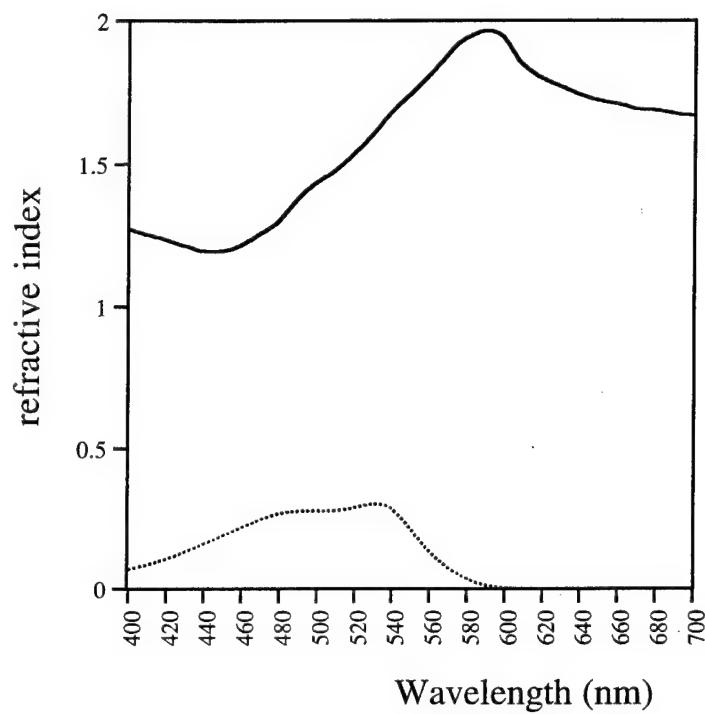




— normal incidence  
····· tilted incidence







— real part  
····· imaginary part

